

METHOD OF MAKING FIBER REINFORCED ELASTOMERIC ARTICLES

BACKGROUND OF THE INVENTION

- 5 The present invention relates generally to a method of manufacturing elastomeric articles having polymer fibers incorporated therein. Examples of such articles may include gloves, condoms, boots, and other elastomeric articles where added strength, comfort, protection (e.g. skin), therapeutic functions, and powder free aspects are desirable characteristics.

There are many prior art arrangements for producing fiber reinforced elastomeric articles.

- 10 Most incorporate an internal lining composed of fibrous material such as cotton flock. Typically flock is composed of finely divided, ground, fibrous particles which are applied as a lining by spraying the flock particles onto an adhesive-covered backing (e.g., the external shell of a glove), for example.

- 15 As one example, an internal glove lining composed of flock provides a smooth, comfortable feel, cushions the hands, absorbs perspiration and keeps the hands dry, insulates against moderate heat and cold without bulk, makes it easier to put on and take off a glove, and has other advantages which increase worker acceptance of a glove.

- Drawbacks to a glove having an internal lining composed of cotton flock (or like fibrous material) are multifaceted: 1) fibers and particles thereof may become detached from the
20 internal lining by abrasion with the surface of the sleeve on the smock or gown worn by the glove wearer or by abrasion with the hand of the glove wearer, and these detached particles can migrate out of the glove, particularly when the glove is removed from the hand of the wearer; 2) fibers like short cotton fibers are not elastomeric, thus are difficult to be coated on disposable gloves based upon latex, nitriles, etc. ; 3) the current
25 commercial flocking process uses glue to make the short cotton fiber to stick, which is essentially a batch process and fibers can not be embedded into the polymer layers

effectively; and 4) current commercial flocked gloves, in some cases, uses powder to enhance the donning and comfort, which are not well accepted among consumers because of allergy and health concerns of small particles.

SUMMARY OF THE INVENTION

- 5 The present invention is drawn to a process for manufacturing a fiber reinforced elastomeric article. Such a process would be capable of providing a lining in which the particles or fibers do not readily detach from the article. Additionally, such a process would enable fibers to be bedded or at least partially bedded into the elastomeric article to enhance the strength of such an article.
- 10 In one aspect of the present invention, a plurality of fibers are deposited onto a former and the former is dipped into a polymer bath containing an elastomeric material. In one embodiment, the fibers are in the form of filaments made by extruding a molten thermoplastic material through a plurality of capillaries, subjecting the molten thermoplastic material to a high velocity hot gas to attenuate the molten thermoplastic material into fine filaments and depositing the still hot filaments onto the former thereby producing a mat of filaments adhering to one another, in the shape of the former surface.
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It is contemplated that the fibers or filaments be placed onto the article at any number of points in the process by for example, dipping the glove into the polymer bath after depositing the filaments onto the former, depositing the filaments onto the former prior to

- 20 dipping the former in a coagulant, depositing the filaments onto the former after dipping the former in a coagulant, and/or dipping the former into the polymer bath prior to depositing the filaments onto the former. Moreover, the process contemplates alternating dipping the former into the polymer bath a series of dips with at least one deposition of filaments.

- 25 The fibers or filaments may be deposited onto the former in a random orientation or in a generally aligned orientation. Moreover, varied quantities of fibers may be deposited onto the former creating regions of different fiber deposit thickness in the elastomeric article.

Such a process may be found useful for the creation of a number of fiber reinforced products for use in industrial applications, surgical procedures, home use, etc. The process may easily be adapted to create gloves and boots, as well as other elastomeric articles.

These and other objects are achieved by the process disclosed and claimed herein.

5 DETAILED DESCRIPTION OF THE INVENTION

In general, an elastomeric article, for example, a glove is formed on a mold, termed a "former". In the case of the glove, the former is hand-shaped. Formers may be made from any suitable material, such as glass, metal, porcelain, or the like. The surface of the former defines at least a portion of the surface of the elastomeric article to be manufactured. It is
10 to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention. As such, in general, one such exemplary elastomeric article of the present invention includes a glove. For ease of illustration and description the specification makes reference to the invention as a glove or gloves. It should, however,
15 be understood that the invention is not limited to gloves alone but includes the broader category of elastomeric articles as well. That being said, in the case of the glove, the surfaces defined include an exterior surface and an interior surface. The interior surface is generally the wearer-contacting surface.

In the process, the former is conveyed through a preheated oven to evaporate any water
20 present. The former may then be dipped into a bath typically containing a coagulant, a powder source, a surfactant, and water. The coagulant may contain calcium ions (from e.g., calcium nitrate) that enable a polymer latex to deposit onto the former. The powder may be calcium carbonate powder, which aids release of the completed glove from the former. The surfactant provides enhanced wetting to avoid forming a meniscus and
25 trapping air between the form and deposited latex, particularly in the cuff area. However, any suitable coagulant composition may be used, including those described in U.S. Patent No. 4,310,928 to Joung, incorporated herein in its entirety by reference. The residual heat evaporates the water in the coagulant mixture leaving, for example, calcium nitrate, calcium carbonate powder, and the surfactant on the surface of the former. Although a

coagulant process is described herein, it should be understood that other processes may be used to form the article of the present invention that do not require a coagulant. For instance, in some embodiments, a solvent-based process may be used.

Once the former is coated, it is then dipped into a polymer bath. The polymer bath is generally a natural rubber latex or a synthetic polymer latex. The polymer present in the bath includes an elastomeric material that forms the body of the glove. In some embodiments, the elastomeric material, or elastomer, includes natural rubber, which may be supplied as a compounded natural rubber latex. Thus, the bath may contain, for example, compounded natural rubber latex, stabilizers, antioxidants, curing activators, organic accelerators, vulcanizers, and the like. In other embodiments, the elastomeric material may be nitrile butadiene rubber, and in particular, carboxylated nitrile butadiene rubber. In other embodiments, the elastomeric material may be a styrene-ethylene-butylene-styrene block copolymer, styrene-isoprene-styrene block copolymer, styrene-butadiene-styrene block copolymer, styrene-isoprene block copolymer, styrene-butadiene block copolymer, synthetic isoprene, chloroprene rubber, polyvinyl chloride, silicone rubber, polyurethane, or a combination thereof.

The stabilizers may include phosphate-type surfactants. The antioxidants may be phenolic, for example, 2,2'-methylenebis (4-methyl-6-t-butylphenol). The curing activator may be zinc oxide. The organic accelerator may be dithiocarbamate. The vulcanizer may be sulfur or a sulfur-containing compound. To avoid crumb formation, the stabilizer, antioxidant, activator, accelerator, and vulcanizer may first be dispersed into water by using a ball mill and then combined with the polymer latex.

During the dipping process, the coagulant on the former causes some of the elastomer to become locally unstable and coagulate onto the surface of the former. The elastomer coalesces, capturing the particles present in the coagulant composition at the surface of the coagulating elastomer. The former is withdrawn from the bath and the coagulated layer is permitted to fully coalesce, thereby forming the glove. The former is dipped into one or more baths a sufficient number of times to attain the desired glove thickness. In some embodiments, the glove may have a thickness of from about 0.001 inches (~0.025mm)

inches (0.102 mm) to about 0.012 inches (0.305 mm). Other embodiments, such as those for use on industrial gloves may be thicker still.

To create a fiber reinforced elastomeric article, a source of fibers must be introduced into the article at one or more points in the above manufacturing process. There are a number 5 of opportunities during the manufacturing process at which time the introduction of fibers is possible. Depending upon the nature of the fibers themselves, the fibers may be applied directly to the former after the former is dried and prior to it being dipped into the coagulant. The fibers may also be applied to the former after the coagulant dip and prior to the former being dipped in the polymer bath itself. In some embodiments of the 10 process, the fibers may be applied to the former after the former is dipped into the polymer bath. At this time, the fibers most easily adhere to the wet elastomeric. Therefore, it is typically at this stage in the process that most flocking operations occur. However, unlike the prior art flocking processes, the present invention is not limited to application 15 of fibers to a wet elastomeric coating. After the application of the fibers, the former may be subjected to a stream of air or some other fluid, typically a pressurized gas or a moving stream of gas from, e.g., a fan, which serves to blow off any excess or loose fibers from the former.

Other possibilities include dipping the glove into the polymer bath both before and after 20 each application of fibers. For example, the glove may first be dipped in the polymer bath, subsequently the fibers are deposited onto the wet elastomeric, and a final seal dip into the polymer bath may be performed as well. This seal dip may be useful to lock the fibers into place on the elastomeric article. This seal dip may serve to prevent piling when the glove is stripped or removed from the former. Piling refers to the condition wherein fiber balls are formed on the glove, or worse, are formed and subsequently detach from the 25 glove due to friction at the fiber coated surface when the glove is removed from the former.

In any event, once the glove has been dipped into the polymer bath and the desired quantity of fibers have been applied, the coated former may then be dipped into a leaching tank in which hot water is circulated to remove the water-soluble components,

such as residual calcium nitrates and proteins contained in the natural rubber latex and excess process chemicals from the synthetic polymer latex. This leaching process may generally continue for about 12 minutes at a water temperature of about 120°F. The fiber reinforced glove is then dried on the former to solidify and stabilize the glove. It should

5 be understood that various conditions, processes, and materials may be used to form the glove. Other layers may be formed by including additional dipping processes. Moreover, additional fibers may be added between dipping processes as well. Such dipping processes and/or fiber applications may be used to incorporate additional features into the glove.

10 The glove is then sent to a curing station where the elastomer is vulcanized, typically in an oven. The curing station initially evaporates any remaining water in the coating on the former and then proceeds to a higher temperature vulcanization. The drying may occur at a temperature of from about 85°C to about 95°C, and the vulcanizing may occur at a temperature of from about 110°C to about 120°C. For example, the glove may be
15 vulcanized in a single oven at a temperature of 115°C for about 20 minutes. Alternatively, the oven may be divided into four different zones with a former being conveyed through zones of increasing temperature. For instance, the oven may have four zones with the first two zones being dedicated to drying and the second two zones being primarily for vulcanizing. Each of the zones may have a slightly higher temperature, for example, the
20 first zone at about 80°C, the second zone at about 95°C, a third zone at about 105°C, and a final zone at about 115°C. The residence time of the former within each zone may be about ten minutes. The accelerator and vulcanizer contained in the latex coating on the former are used to crosslink the elastomer. The vulcanizer forms sulfur bridges between different elastomer segments and the accelerator is used to promote rapid sulfur bridge
25 formation.

Upon being cured, the former may be transferred to a stripping station where the glove is removed from the former. The stripping station may involve automatic or manual removal of the glove from the former. For example, in one embodiment, the glove is manually removed and turned inside out as it is stripped from the former. By inverting
30 the glove in this manner, the exterior of the glove on the former becomes the inside

surface of the glove. It should be understood that any method of removing the glove from the former may be used, including a direct air removal process that does not result in inversion of the glove.

The solidified glove, or a plurality of solidified gloves, may then subjected to various post-
5 formation processes, including application of one or more treatments to at least one surface of the glove. For instance, the glove may be halogenated to decrease tackiness of the interior surface. The halogenation (e.g., chlorination) may be performed in any suitable manner, including: (1) direct injection of chlorine gas into a water mixture, (2) mixing high density bleaching powder and aluminum chloride in water, (3) brine
10 electrolysis to produce chlorinated water, and (4) acidified bleach. Examples of such methods are described in U.S. Patent Nos. 3,411,982 to Kavalir; 3,740,262 to Agostinelli; 3,992,221 to Homsy, et al.; 4,597,108 to Momose; and 4,851,266 to Momose, 5,792,531 to Littleton, et al., which are each herein incorporated by reference in their entirety. In one embodiment, for example, chlorine gas is injected into a water stream and then fed into a
15 chlorinator (a closed vessel) containing the glove. The concentration of chlorine may be altered to control the degree of chlorination. The chlorine concentration may typically be at least about 100 parts per million (ppm). In some embodiments, the chlorine concentration may be from about 200 ppm to about 3500 ppm. In other embodiments, the chlorine concentration may be from about 400 ppm to about 1200 ppm. In yet other
20 embodiments, the chlorine concentration may be about 800 ppm. The duration of the chlorination step may also be controlled to vary the degree of chlorination and may range, for example, from about 1 to about 20 minutes. In some embodiments, the duration of chlorination may be about 10 minutes.

Still within the chlorinator, the chlorinated glove or gloves may then be rinsed with tap
25 water at about room temperature. This rinse cycle may be repeated as necessary. The gloves may then be tumbled to drain the excess water.

A lubricant composition may then be added into the chlorinator, followed by a tumbling process that lasts for about five minutes. The lubricant forms a layer on at least a portion of the interior surface to further enhance donning of the glove. In one embodiment, this

lubricant may contain a silicone or silicone-based component. As used herein, the term "silicone" generally refers to a broad family of synthetic polymers that have a repeating silicon-oxygen backbone, including, but not limited to, polydimethylsiloxane and polysiloxanes having hydrogen-bonding functional groups selected from the group consisting of amino, carboxyl, hydroxyl, ether, polyether, aldehyde, ketone, amide, ester, and thiol groups. In some embodiments, polydimethylsiloxane and/or modified polysiloxanes may be used as the silicone component in accordance with the present invention. For instance, some suitable modified polysiloxanes that may be used in the present invention include, but are not limited to, phenyl-modified polysiloxanes, vinyl-modified polysiloxanes, methyl-modified polysiloxanes, fluoro-modified polysiloxanes, alkyl-modified polysiloxanes, alkoxy-modified polysiloxanes, amino-modified polysiloxanes, and combinations thereof. Examples of commercially available silicones that may be used with the present invention include DC 365 available from Dow Corning Corporation (Midland, Michigan), and SM 2140 available from GE Silicones (Waterford, New York). However, it should be understood that any silicone that provides a lubricating effect may be used to enhance the donning characteristics of the glove. The lubricant solution is then drained from the chlorinator and may be reused if desired. It should be understood that the lubricant composition may be applied at a later stage in the forming process, and may be applied using any technique, such as dipping, spraying, immersion, printing, tumbling, or the like.

The coated glove may then be put into a tumbling apparatus or other dryer and dried for about 10 to about 60 minutes (e.g., 40 minutes) at from about 20°C to about 80°C (e.g., 40°C). The glove may then be inverted to expose the exterior surface, which may then be dried for about 20 to about 100 minutes (e.g., 60 minutes) at from about 20°C to about 80°C (e.g., 40°C).

After the various processes described above, the glove may be inverted (if needed) to expose the exterior surface of the elastomeric article, for example, the glove. Any treatment, or combination of treatments, may then be applied to the exterior surface of the glove. Individual gloves may be treated or a plurality of gloves may be treated simultaneously. Likewise, any treatment, or combination of treatments, may be applied to

the interior surface of the glove. Any suitable treatment technique may be used, including for example, dipping, spraying, immersion, printing, tumbling, or the like.

Regarding the fibers added to the elastomeric article during the manufacturing process, any suitable fibrous material may be used. Such fibrous material may include natural fibers, synthetic fibers, and mixtures thereof, including meltblown and spunbond. Suitable fibers include meltspun filaments, staple fibers, pulp fibers, meltspun multicomponent filaments, and the like. Moreover, the fibers may also include various other materials such as elastomeric components. Synthetic fibers or filaments may have any suitable morphology including hollow or solid, straight or crimped, single component, conjugate or biconstituent fibers or filaments, and blends or mixtures of such fibers and/or filaments, as are well known in the art.

As used herein, the term "biconstituent fibers" refers to fibers which have been formed from at least two polymers extruded from the same extruder as a blend. Biconstituent fibers do not have the various polymer components arranged in relatively constantly positioned distinct zones across the cross-sectional area of the fiber and the various polymers are usually not continuous along the entire length of the fiber, instead they usually form fibrils or protofibrils that start and end at random. Biconstituent fibers are sometimes referred to as multiconstituent fibers. Fibers of this general type are discussed in, for example, U.S. Patent Nos. 5,108,827 and 5,294,482 to Gessner. Biconstituent fibers are also discussed in the textbook Polymer Blends and Composites by John A. Manson and Leslie H. Sperling, copyright 1976 by Plenum Press., a division of Plenum Publishing Corporation of New York, ISBN 0-306-30831-2, at pages 273 through 277.

As used herein, the term "conjugate fibers" refers to fibers which have been formed from at least two polymers extruded from separated extruders but spun together to form one fiber. Conjugate fibers are also sometimes referred to as multicomponent or bicomponent fibers. The polymers are usually different from each other though conjugate fibers may be monocomponent fibers. The polymers are arranged in substantially constantly positioned distinct zones across the cross-section of the conjugate fibers and extend continuously along the length of the conjugate fibers. The configuration of such a conjugate fiber may

be, for example, a sheath/core arrangement, wherein one polymer is surrounded by another or may be a side by side arrangement, a pie arrangement or an "islands-in-the-sea" arrangement. Conjugate fibers are taught by U.S. Patent Nos. 5,108,820 to Kaneko et al., and 4,795,668 to Krueger et al., 5,336,552 to Strack et al. Conjugate fibers are also 5 taught in U.S. Patent No. 5,382,400 to Pike et al. and may be used to produce crimp in the fibers by using the differential rates of expansion and contraction of the two (or more) polymers. Crimped fibers may also be produced by mechanical means and by the process of German Patent DT 25 13 251 A1. For two component fibers, the polymers may be present in ratios of 75/25, 50/50, 25/75, or any other desired ratios. The fibers may also 10 have shapes such as those described in U.S. Patent Nos. 5,277,976 to Hogle et al. 5,466,410 to Hill, 5,069,970 to Largman et al., and 5,057,368 to Largman et al., which describe fibers with unconventional shapes.

As used herein, the term "filament" refers to a generally continuous strand that has a large ratio of length to diameter, such as, for example, a ratio of 1000 or more.

- 15 As used herein, "meltblown fibers" refer to fibers formed by extruding a molten thermoplastic material through a plurality of fine, usually circular, die capillaries as molten threads or filaments into converging high velocity, usually hot, gas (e.g. air) streams that attenuate the filaments of thermoplastic material to reduce their diameter, which may be to microfiber diameter. Thereafter, the meltblown fibers are carried by the 20 high velocity gas stream and are deposited on a collecting surface to form a mat or web of randomly disbursed meltblown fibers. Such a process is disclosed, for example, in U.S. Patent No. 3,849,241 to Butin et al. Meltblown fibers are microfibers which may be continuous or discontinuous, are generally smaller than 10 microns in average diameter, and are generally tacky when deposited on a collecting surface.
- 25 As used herein, "spunbond fibers" refer to small diameter fibers which are formed by extruding molten thermoplastic material as filaments from a plurality of fine, usually circular capillaries of a spinneret with the diameter of the extruded filaments then being rapidly reduced as by, for example, in U.S. Patent Nos. 4,340,563 to Appel et al., 3,692,618 to Dorschner et al., 3,802,817 to Matsuki et al., 3,338,992 to Kinney, 3,341,394 to Kinne,

3,502,763 to Hartman, and 3,542,615 to Dobo et al. Spunbond fibers are generally not tacky when they are deposited on a collecting surface. Spunbond fibers are generally continuous and have average diameters (from a sample of at least 10) larger than 7 microns, and more particularly, between about 10 and 40 microns.

5 Regardless of their diameter, the synthetic fibers used in the present invention may be formed from a variety of thermoplastic polymers where the term "thermoplastic polymer" refers to a long chain polymer that repeatedly softens when exposed to heat and substantially returns to its original state when cooled to ambient temperature. As used herein with respect to fibers and or filaments, the term "polymer" generally includes, but
10 is not limited to, homopolymers, copolymers, such as for example, block, graft, random, and alternating copolymers, terpolymers, etc., and blends and modifications thereof. As used herein, the term "blend" means a mixture of two or more polymers. Furthermore, unless otherwise specifically limited, the term "polymer" shall include all possible geometrical configurations of the molecule. These configurations include, but are not
15 limited to, isotactic, synditactic, and random symmetries.

Exemplary thermoplastics include, without limitation, poly(vinyl) chlorides, polyesters, polyamides, polyfluoro-carbons, polyolefins, polyurethanes, polystyrenes, poly(vinyl) alcohols, caprolactams, and copolymers of the foregoing, and elastomeric polymers such as elastic polyolefins, copolyether esters, polyamide polyether block copolymers, ethylene
20 vinyl acetates (EVA), block copolymers having the general formula A-B-A' or A-B like copoly(styrene/ethylene-butylene), styrene-poly(ethylene-propylene)-styrene, styrene-poly(ethylene-butylene)-styrene, (polystyrene/poly(ethylene-butylene)/polystyrene, poly(styrene/ethylene-butylene/styrene), A-B-A-B tetrablock copolymers and the like.

Many polyolefins are available for fiber production, for example polyethylenes such as
25 Dow Chemical's PE XU 61800.41 linear low density polyethylene ("LLDPE") and 25355 and 12350 high density polyethylene ("HDPE") are such suitable polymers. Fiber-forming polypropylenes include Exxon Chemical Company's Escorene® PD 3445 polypropylene and Montell Chemical Co.'s PF-304 and PF-015. Many other conventional polyolefins are commercially available and include polybutylenes and others.

Examples of polyamides and their methods of synthesis may be found in "Polymer Resins" by Don E. Floyd (Library of Congress Catalog No. 66-20811, Reinhold Publishing, New York, 1966). Particularly commercially useful polyamides are nylon-6, nylon 6,6, nylon-1 1 and nylon-1 2. These polyamides are available from a number of sources such as

- 5 Emser Industries of Sumter, South Carolina (Grilon® & Grilamid® nylons), Atochem Inc. Polymers Division of Glen Rock, New Jersey (Rilsan® nylons), Nyltech of Manchester, New Hampshire (grade 2169, Nylon 6), and Custom Resins of Henderson, Kentucky (Nylene 401 -D), among others.

As stated above, staple fibers may be added. In some embodiments, staple fibers may be
10 used to increase the strength, bulk, softness and smoothness of the article. Staple fibers may include, for instance, various polyolefin fibers, polyester fibers, nylon fibers, polyvinyl acetate fibers, cotton fibers, rayon fibers, nonwoody plant fibers, and mixtures thereof. In general, staple fibers are typically longer than pulp fibers. For instance, staple fibers typically have fiber lengths of 5 mm and greater.

- 15 The fibers used in the present invention may also be curled or crimped. The fibers may be curled or crimped, for instance, by adding a chemical agent to the fibers or subjecting the fibers to a mechanical process. Curled or crimped fibers may create more entanglement and void volume between the fibers and further increase the amount of fibers oriented in the z-direction as well as increase strength properties.
- 20 As stated, the type of synthetic fibers used in the invention include bicomponent fibers. Bicomponent fibers are fibers that can contain two materials such as but not limited to in a side by side arrangement, in a matrix-fibril arrangement, wherein a core polymer has a complex cross-sectional shape, or in a core and sheath arrangement. In a core and sheath arrangement, generally the sheath polymer has a lower melting temperature than the core
25 polymer to facilitate thermal bonding of the fibers. For instance, the core polymer, in one embodiment, may be nylon or a polyester, while the sheath polymer may be a polyolefin such as polyethylene or polypropylene. Such commercially available bicomponent fibers include "CELBOND" fibers marketed by the Hoechst Celanese Company.

Besides or in addition to synthetic fibers, pulp fibers may also be added to the article. The

pulp fibers used may be soft wood fibers having an average fiber length of greater than 1 mm, and particularly from about 2 to 5 mm based on a length weighted average. Such fibers may include northern softwood craft fibers, redwood fibers, and pine fibers. Secondary fibers obtained from recycled materials may also be used. In addition, 5 hardwood pulp fibers, such as eucalyptus fibers, may also be utilized in the present invention.

Besides the above-mentioned fibers, thermomechanical pulp fibers may also be added to the base web. Thermomechanical pulp, as is known to one skilled in the art, refers to pulp that is not cooked during the pulping process to a lesser extent than conventional pulps.

10 Thermomechanical pulp tends to contain stiff fibers and has higher levels of lignin. Thermomechanical pulp may be added to the base web of the present invention in order to create an open pore structure, thus increasing bulk and absorbency and improving resistance to wet collapse.

15 The pulp fibers may be added generally simultaneously with synthetic fibers in a process known as a coform process. In general, "coform" means a process in which at least one meltblown die is arranged near a chute through which other materials are added to the web while it forms. Such other materials may include, for example, pulp, superabsorbent particles, cellulose, or staple fibers. Coform processes are described in U.S. Pat. Nos. 4,818,464 to Lau and 4,100,324 to Anderson et al., which are incorporated by reference.

20 As described above, besides containing various nonelastic materials, the fibers used in the present invention may also contain an elastomeric component. In general, any material known in the art to possess elastomeric characteristics may be used in the present invention as an elastomeric component. Suitable elastomeric resins include block copolymers having the general formula A-B-A' or A-B, where A and A' are each a 25 thermoplastic polymer endblock which contains a styrenic moiety such as a poly(vinyl arene) and where B is an elastomeric polymer midblock such as a conjugated diene or a lower alkene polymer. Block copolymers for the A and A' blocks, and the present block copolymers are intended to embrace linear, branched and radial block copolymers. In this regard, the radial block copolymers may be designated (A-B)_m-X, wherein X is a

- polyfunctional atom or molecule and in which each (A-B)_m- radiates from X in a way that A is an endblock. In the radial block copolymer, X may be an organic or inorganic polyfunctional atom or molecule and m is an integer having the same value as the functional group originally present in X. It is usually at least 3, and is frequently 4 or 5, but
- 5 not limited thereto. Thus, in the present invention, the expression "block copolymer," and particularly "A-B-A" and "A-B" block copolymer, is intended to embrace all block copolymers having such rubbery blocks and thermoplastic blocks as discussed above, which may be extruded (e.g., by meltblowing), and without limitation as to the number of blocks.
- 10 The elastomeric component may be formed from, for example, elastomeric (polystyrene/poly(ethylene-butylene)/ polystyrene) block copolymers. Commercial examples of such elastomeric copolymers are, for example, those known as KRATON® materials which are available from Shell Chemical Company of Houston, Texas. KRATON® block copolymers are available in several different formulations, a number of
- 15 which are identified in U.S. Patent Nos. 4,663,220, 4,323,534, 4,834,738, 5,093,422 and 5,304,599, which are incorporated herein by reference.
- Polymers composed of an elastomeric A-B-A-B tetrablock copolymer may also be used in the practice of this invention. Such polymers are discussed in U.S. Patent No. 5,332,613 to Taylor et al. In such polymers, A is a thermoplastic polymer block and B is an isoprene monomer unit hydrogenated to substantially a poly(ethylenepropylene) monomer unit.
- 20 An example of such a tetrablock copolymer is a styrene-poly(ethylene-propylene)-styrenepoly(ethylene-propylene) or SEPSEP elastomeric block copolymer available from the Shell Chemical Company of Houston, Texas under the trade designation KRATON® G-1657.
- 25 Other exemplary elastomeric materials which may be used include polyurethane elastomeric materials such as, for example, those available under the trademark ESTANE® from B.F. Goodrich & Co. or MORTHANE® from Morton Thiokol Corp., polyester elastomeric materials such as, for example, those available under the trade designation HYTREL® from E. I. DuPont De Nemours & Company, and those known as

ARNITEL®, formerly available from Akzo Plastics of Arnhem, Holland and now available from DSM of Sittard, Holland.

Other suitable materials include polyester block amide copolymers such as those available under the trade designation PEBA^X® from ELF Atochem Inc. of Glen Rock, New Jersey.

- 5 Examples of the use of such polymers may be found in U.S. Patent Nos. 4,724,184, 4,820,572 and 4,923,742 to Killian. Elastomeric polymers may also include copolymers of ethylene and at least one vinyl monomer such as, for example, vinyl acetates, unsaturated aliphatic monocarboxylic acids, and esters of such monocarboxylic acids. The elastomeric copolymers and formation of elastomeric nonwoven webs from those elastomeric 10 copolymers are disclosed in, for example, U.S. Patent No. 4,803,117. Thermoplastic copolyester elastomers including copolyetheresters may also be used. Commercial examples of such copolyester materials are, for example, those known as ARNITEL®, formerly available from Akzo Plastics of Arnhem, Holland and now available from DSM of Sittard, Holland, or those known as HYTREL® which are available from E.I. DuPont de 15 Nemours of Wilmington, Delaware. Formation of an elastomeric nonwoven web from polyester elastomeric materials is disclosed in, for example, U.S. Patent No. 4,741,949 to Norman et al. and U.S. Patent No. 4,707,398 to Boggs.

Elastomeric olefin polymers are also available from Exxon Chemical Company of Baytown, Texas under the trade name ACHIEVE® for polypropylene based polymers and 20 EXACT® and EXCEED® for polyethylene based polymers. Dow Chemical Company of Midland, Michigan has polymers commercially available under the name ENGAGE®. Exxon generally refers to their metallocene catalyst technology as "single site" catalysts while Dow refers to theirs as "constrained geometry" catalysts under the name INSIGHT® to distinguish them from traditional Ziegler-Natta catalysts which have 25 multiple reaction sites.

For instance, as stated above, in one embodiment of an elastomeric article containing fibers, meltblown fibers are used. The meltblown fibers may be continuous or discontinuous. Meltblown fibers have been conventionally made by extruding a thermoplastic polymeric material through a die to form fibers or filaments. As the molten

- polymer fibers exit the die, a high pressure fluid, such as heated air or steam, attenuates the molten polymer fibers to form fine filaments. Surrounding cool air is induced into the hot air stream to cool and solidify the filaments. The filaments are then randomly deposited onto the former to form a web or mat. When the fibers are deposited on the
- 5 former, they are still tacky and stick to the surface of the former as well as to each other. Therefore when applying tacky fibers or filaments, as in a meltblown process, the fibers may be deposited directly onto the former prior to or after the coagulant dip. The fibers may also be applied directly to the wet elastomeric coating after the former is dipped into the polymer bath.
- 10 Besides meltblown fibers, it should be understood that other processes may be used as well. One such process includes the application of spunbond fibers. Spunbond fibers are typically produced by heating a thermoplastic polymeric resin to at least its softening temperature, then extruding it through a spinnerette to form continuous fibers or filaments, which can be subsequently fed through a fiber draw unit. From the fiber draw
- 15 unit the filaments are spread onto the former in a manner similar to that used in the meltblown application. However, since spunbond filaments are not tacky they must be applied to a wet or tacky surface. In one application, the spunbond filaments are applied directly to the still wet elastomeric surface coating the former after the former is removed from the polymer bath.
- 20 In addition to the above polymeric fibers, pulp fibers and/or staple fibers may be added as disclosed above. As an example, one method of adding pulp fibers to the polymeric fibers is to extrude the thermoplastic polymeric resin through a die or spinnerette to form continuous fibers such as described in the meltblown application above. The fibers are attenuated into filaments by the use of a primary fluid stream of heated air or steam. This
- 25 primary fluid stream is merged with a secondary fluid stream containing individualized wood pulp fibers. As the two streams merge, the polymeric fibers are integrated with the pulp fibers in a single step. This process may also be used to add staple fibers, superabsorbent particles, cellulose, and other fibers and/or particles as well. Referring again to pulp fibers, in some desirable embodiments, the individualized wood pulp fibers
- 30 may typically have a length of about 0.5 to 10 millimeters and a length-to-maximum

width ratio of about 10/1 to 400/1. A typical cross-section may have an irregular width of 30 microns and a thickness of 5 microns.

It is contemplated that the method of making fiber reinforced elastomeric articles in accordance with the present invention will be tailored and adjusted by those of ordinary

5 skill in the art to accommodate various desirable features. Accordingly, while this invention has been described by reference to certain specific embodiments and examples, it will be understood that this invention is capable of further modifications. This application is, therefore, intended to cover any variations, uses or adaptations of the invention following the general principles thereof, and including such departures from
10 the present disclosure as come within known or customary practice in the art to which this invention pertains and fall within the limits of the appended claims.